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A Rapid Method for the Determination of ^{137}Cs in Seawater

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ABSTRACT

A method is developed to measure ^{137}Cs in seawater. It entails the use of silica gel impregnated with hexacyanoferrates as an ion-exchanger to concentrate ^{137}Cs from large volumes of seawater, followed by gamma-ray spectrometry with a high efficiency HPGe detector. Both laboratory experiments and field operation resulted in satisfactory recovery of ^{137}Cs. Compared with the traditional pre-concentration method using AMP as the scavenger, this method is more rapid, more cost-effective, and can be more easily performed aboard ships.

(Key words: ^{137}Cs, Seawater, Copper hexacyanoferrates)

1. INTRODUCTION

Cs-137 is a fission product with a long half-life which can be released into natural environments from atomic bomb tests, nuclear accidents, and nuclear waste disposal. As an element in the alkali group, Cs commonly exists and migrates in the monovalent state in aquatic environments. As such, the determination of ^{137}Cs in aqueous systems can be applied to monitor the release of nuclear wastes and radiation contamination of the environment. Furthermore, because the major source of ^{137}Cs in the vast ocean is from the atmosphere, this nuclide can be used as a tracer for studying oceanic processes. However, because the concentration of ^{137}Cs in natural waters is usually very low, its application is hampered by the volume requirement. Overcoming this difficulty requires improvements in the concentration and analytical methods.

The concentration of ^{137}Cs in seawater is so low ($2.9\text{-}6.6 \times 10^{-9}$ M; Gaur 1996) that pre-concentration of this nuclide from large volume samples is required before radioactivity analysis. Traditionally, the most common method has been to acidify seawater samples to about pH 1.5 followed by adsorption of ^{137}Cs onto ammonium molybdophosphate (AMP). This method also involves adding known amounts of stable Cs as the carrier and yield determinant. After sufficient stirring of the sample to effect the adsorption of Cs onto AMP, the Cs-AMP is

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separated from the sample solution by gravitational settling and centrifuge. Collection of the Cs-AMP is followed by sequence of procedures, including EDTA-complexation and ion exchange, to separate the Cs from other alkali metals. Finally, the Cs is co-precipitated with H_2PtCl_6, which is used as a carrier phase. The recovery of the Cs can be determined by atomic absorption spectrometry or by gravimetric measurement of H_2PtCl_6. Finally, the activity of ^{137}Cs is assayed by either beta counting or gamma spectrometry.

The radiochemical method described above is not only time-consuming but also laborious. Besides, it is very difficult to perform the pre-concentration method at sea, especially when conditions are rough. All these greatly limit the number of samples that can be collected and processed at sea, or brought back to the shore-based laboratory.

The purpose of this study is to devise a method for rapid collection and processing of large-volume samples at sea, followed by non-destructive analysis of ^{137}Cs by gamma spectrometry using a high-efficiency HPGe detector.

2. BACKGROUND

In wake of the development of ion-exchangers over the past several decades, various exchangers have been applied to pre-concentrate ^{137}Cs in water samples. The exchangers employed include organic resin, liquid ion exchanger (i.e., solvent extractants) and inorganic ion exchangers (Gaur 1996). Although organic resin is very effective at removing Cs, it is not capable of differentiating Cs from other alkali metals, which are far more abundant in seawater. In comparison, inorganic ion exchangers have a higher selectivity for Cs and are stable in seawater; therefore they are often used for the pre-concentration of ^{137}Cs in seawater.

There are natural and artificially synthesized inorganic ion exchangers. The former includes zeolites, clay minerals and feldspars, while the latter includes hydrous oxides, acidic salts of multivalent metals, heteropolyacid salts, hexacyanoferrates, and synthetic aluminosilicates (Veselý and Pekárek 1972; Teng et al. 1999). Although natural ion exchangers are cheap, it is difficult to control their quality and purity. Therefore, they may be cost-effective for large-scale industrial applications but are not suitable for quantitative analysis in the laboratory. As for artificial ion exchangers, ammonium 12-molybdophosphate (AMP; $[(NH_4)_3Mo_{12}O_{40}(xH_2O)]$), synthetic zeolites and hexacyanoferrates have all been used for this purpose. Because AMP is in microcrystalline form, it impedes the flow of sample solution through the ion exchange column and hence is not suitable for large-volume seawater samples. Synthetic zeolites are not appropriate for concentrating Cs from seawater, either, because they do not exclude Na and K (Huang et al. 1994). Therefore, for rapid collection and processing of large-volume seawater samples at sea, the above two types of synthetic ion exchangers should not be considered.

Compared with the other two types of synthetic ion exchangers, hexacyanoferrates have the advantages of being both selective for Cs and easy to prepare. Hexacyanoferrates are compounds of various transition elements such as Co, Ni, Cu and Zn. Although all of them perform well in pre-concentrating Cs from seawater (Gaur 1996 and references therein), Cu-hexacyanoferrate exhibits the best stability in seawater. Therefore, our attention is focussed on this type of material for further evaluation.

The hexacyanoferrate ion exchanger can be prepared in three forms: intrinsic, supported, and composite (Teng et al. 1999). This work will follow that of Terada et al. (1970) using silica gel as the supporting bed for the Cu-hexacyanoferrate ion exchanger.

3. EXPERIMENTAL

3.1 Reagents and Standards

3.1.1 Radionuclide standard

To calibrate the energy and efficiency spectra of the HPGe detector, three radionuclide standards were used: ^{7}Be (ORNL S/M 054911), ^{137}Cs (NIST SRM-4233) and ^{152}Eu (NIST SRM-4370C). They were added to an equal amount of the ion exchanger and counted with the same geometry (hence efficiency) as the samples.

3.1.2 Silica gel and other chemicals

The silica gel used in this study is chromatographic grade (MERCK Silica gel 60, 0.2-0.5 mm). All other chemicals used are of GR grade, and include potassium hexacyanoferrate (II) trihydrate ($K_4Fe(CN)_6$ ($3H_2O$) and copper(II) chloride ($CuCl_2$).

3.2 Equipment and Apparatus

3.2.1 Filtration system

This is used to separate suspended particles from solution by pressure-filtering seawater, using a Masterflex® wriggle pump, through a teflon-lined filter holder (Satorius PTFE). The filter membrane is made of polycarbonate, with a nominal pore size of 0.4 μ m and diameter of 142 mm.

3.2.2 Ion exchange column

This part consists of a polyethylene column (I.D. = 1.6 cm, length = 15 cm) packed with 5 g of the exchanger and connected to a peristaltic pump.

3.2.3 Counting system

The counting system includes a 100% efficiency (relative to 3(3 NaI) HPGe detector (EG&G ORTEC GMX-100265-P) interfaced to a digital gamma-ray spectrometer (DSPec®).

3.3. Preparation of Silica Gel Supported Copper Hexacyanoferrates

The procedures to prepare the silica-gel-supported copper hexacyanoferrates used in this work are as follows.

(1) Immerse 100 g of silica gel into an adequate amount of 0.1 M potassium hexacyanoferrate (II) trihydrate ($K_4Fe(CN)_6$ ($3H_2O$) in a 2-liter beaker and stir for 1 hour, using a magnetic stirrer.

(2) Dry up and then immerse the silica gel in 0.2 M copper chloride ($CuCl_2$) solution. Stir for one hour to effect the copper hexacyanoferrate precipitation as coatings on the silica gel.

(3) Rinse the silica gel with distilled water to remove excess, loose copper hexacyanoferrate. The treated silica gel is then heated at 80°C in an oven for about 24 hours to remove moisture.

3.4 Chemical Composition of the Copper Hexacyanoferrate Coating on the Treated Silica Gel

In order to test the consistency and homogeneity of the chemical composition of the copper hexacyanoferrate coating, each batch of the ion exchanger was dissolved with a mixture of mineral acids (HCl and HF), and analyzed for K, Fe, and Cu using a flame atomic absorption spectrometer (Perkin Elmer 3110). The results are given in Table 1.

According to Bellomo (1970), there are three forms of copper hexacyanoferrates, formed by the reactions as below.

$$2Cu^{2}+ + Fe(CN)_6^{4-} \rightarrow Cu_2Fe(CN)_6,$$

$$Cu^{2+} + 2K^+ + Fe(CN)_6 \rightarrow K_2CuFe(CN)_6,$$

$$3Cu_2Fe(CN)_6 + 4K^+ + Fe(CN)_6^{4-} \rightarrow 2K_2Cu_3[Fe(CN)_6]_2.$$

When K^+ is present, $K_2Cu_3[Fe(CN)_6]_2$ is the primary form of hexacyanoferrates, which has a Cu to Fe molar ratio of 3 to 2. The data in Table 1 show very limited variation in the Cu to Fe molar ratio between different batches of hexacyanoferrates. The mean Cu/Fe ratios (1.5-1.6) are consistent with that reported by Bellomo (1970), suggesting that the chemical reaction involved in our procedures can be mainly described by the third reaction given above. However, it should be noted that the coating efficiency varies between batches; the amount of hexacyanoferrates coated onto silica gel in the second batch was about half that in the first batch.

3.5 Determination of ^{137}Cs in Seawater Samples

Seawater samples were collected using 20-l Go-Flo bottles attached to a CTD rosette. Samples were collected during upcast, with 2-3 bottles fired at each depth to obtain 40-60 l samples. Immediately following collection, each seawater sample was pumped through a 0.4-μm filter paper followed by two ion exchange columns at a flow rate of 20-30 l/hr. The ion exchanger from each column was then transferred into a plastic jar, dried at 70°C in an oven, and then counted with an HPGe detector interfaced to a digital spectrometer.

Table 1. Chemical composition of the copper hexacyanoferrate coating on the treated silica gel.

Samp. No.	Cu			Fe			K			Cu : Fe : K		
	ug/g			ug/g			ug/g					
1[a]	5293	±	45	3140	±	36	1374	±	81	48	32	20
2[a]	5177	±	6	3090	±	106	1434	±	18	47	32	21
3[a]	5260	±	13	3236	±	35	1390	±	111	47	33	20
4[a]	5333	±	20	3246	±	110	1498	±	60	47	32	21
5[b]	3358	±	17	1777	±	163	551	±	55	54	32	14
6[b]	3267	±	7	1749	±	8	508	±	63	54	33	14
7[b]	3219	±	10	1847	±	102	641	±	29	51	33	16
8[b]	3173	±	20	1699	±	34	607	±	30	52	32	16

average of a	1.5	1.0	0.6
average of b	1.6	1.0	0.5

[a] silica gel supported ferrocyanide prepared on Mar. 2, 1999.

[b] silica gel supported ferrocyanide prepared on Mar. 6, 1999.

Calibration of the HPGe detector was performed using a standard prepared by spiking 5 g of the ion exchanger with known activities of ^{137}Cs, ^{7}Be and ^{152}Eu. The absolute counting efficiency at the 661.62 keV photon energy of ^{137}Cs was 6.57% and the peak resolution was 1. 71 keV (FWHM).

It is conceivable that the adsorption efficiency of seawater 137Cs onto the ion exchanger depends on the flow rate and the weight and surface area of the exchanger, which vary between samples. To circumvent this problem, two columns are placed in series (Fig. 1) so that the absolute adsorption efficiency (E) and the concentration of ^{137}Cs (A) for each sample can be calculated by:

$$E = \frac{[F]-[B]}{F},$$

$$A = \frac{[F]}{E \cdot V}.$$

Where $[F]$ and $[B]$ are the activity of ^{137}Cs in the front cartridge and the back cartridge, respectively, and V is the volume of seawater pumped through the cartridges.

4. RESULTS AND DISCUSSION

4.1 Preliminary Study in the Laboratory

In order to test the adsorption efficiency of ^{137}Cs onto copper hexacyanoferrates, a batch experiment was performed as described below. A known activity of ^{137}Cs (26.4 ± 0.2 dpm) was used to spike 100 ml of seawater (collected by R/V Ocean Researcher-I from cruise OR413, Station 15, surface water). To the spiked seawater was then added copper hexacyanoferrate synthesized from 5 ml each of 0.2M $CuCl_2$ and 0.1M $K_4Fe(CN)_6$. Table 2 shows that ^{137}Cs can be quantitatively removed from seawater in 2-3 minutes.

Besides the batch experiment described above, the reliability of the column operation was also tested in the laboratory, as follows. A known activity of ^{137}Cs (165.3 ± 1.1 dpm) was used to spike 4 l of seawater (from R/V Ocean Researcher-I from cruise OR542, Station 18, 200 m). Three pairs of the ion exchange columns were used to process the spiked seawater at a flow rate of 0.5 l/min. The calculated adsorbing efficiencies are 88.5± 1.2% (n=3; Table 3). The calculated ^{137}Cs activities are 0.992± 0.013 (n=3) of the actual value (41.3±0.4 dpm/l), and demonstrate that this method is satisfactory and should work well with real samples.

4.2 Field Experiments

Real samples for this study were collected on board R/V Ocean Researcher-I on her 542nd and 551st cruises to the southern Taiwan Strait and the East China Sea, respectively. The sampling sites are shown in Fig. 2. At one of the stations, OR542-18, where the water depth is ~1500 m, samples were collected at the surface, 200 m, 500 m, 700 m and 1000 m below the

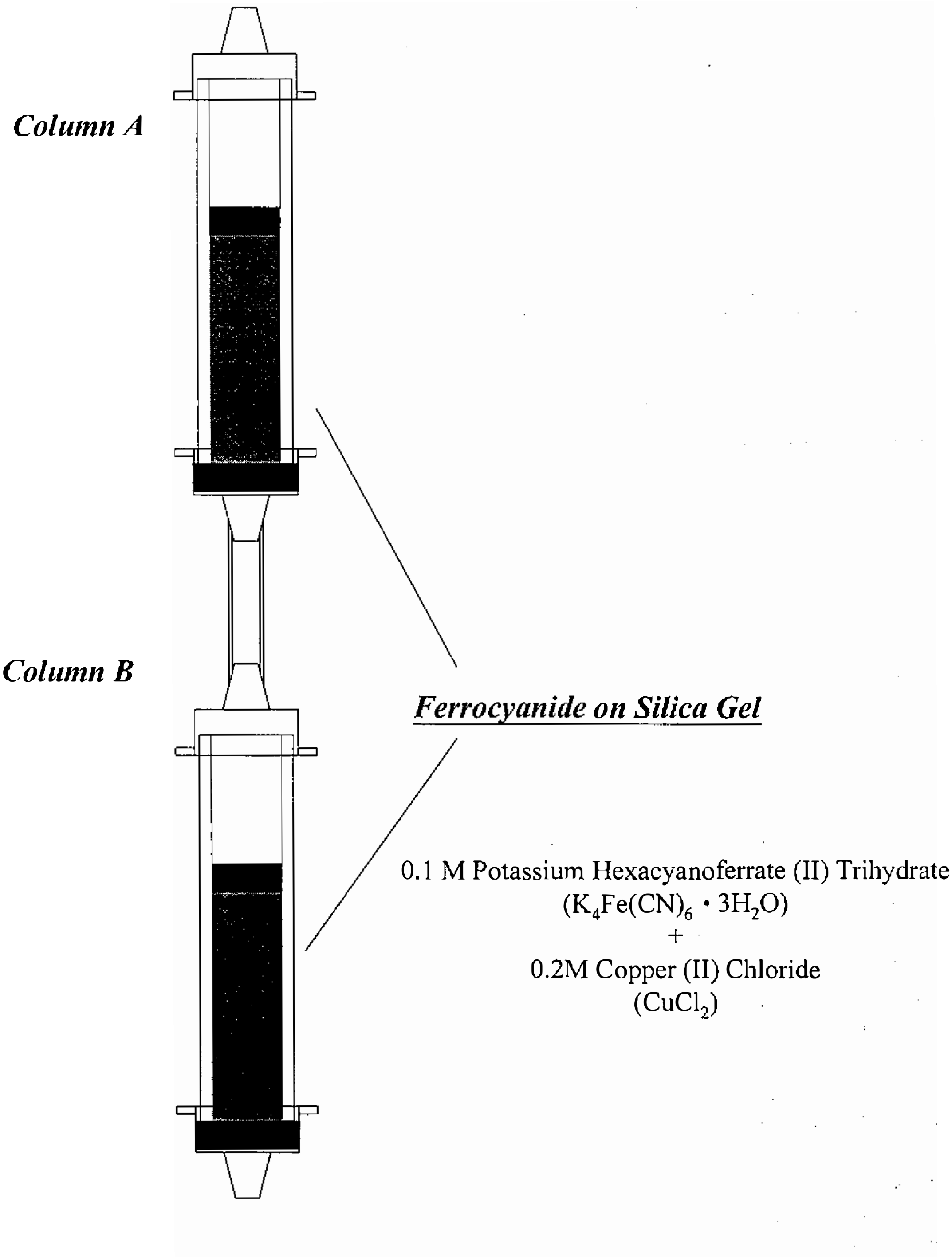

Fig. 1. The ion-exchange column system for ^{137}Cs analysis of seawater in this study.

Table 2. Time variation of adsorption of ^{137}Cs on copper hexacyanoferrate.

	Time (minute)	Calculated ^{137}Cs (dpm)	Actual ^{137}Cs (dpm)	Calculated/Actual activity ratio
1	2.5	26.7 ± 2.1	26.4 ± 0.2	1.01 ± 0.08
2	16	28.8 ± 2.3	26.4 ± 0.2	1.09 ± 0.09
3	41	24.9 ± 4.4	26.4 ± 0.2	0.94 ± 0.17
4	68	27.9 ± 4.9	26.4 ± 0.2	1.05 ± 0.19

Table 3. Results of the reliability test of the column operation.

No.	Cs-137 (dpm)	Effic. of Column %	Calculated activity of Cs-137 dpm	Calculated/Actual activity ratio
1A	145.0 ± 2.3	88.33	164.2 ± 4.6	0.993 ± 0.028
1B	16.9 ± 0.8			
2A	144.6 ± 2.4	87.13	165.9 ± 4.9	1.004 ± 0.029
2B	18.6 ± 0.7			
3A	145.5 ± 3.5	89.97	161.7 ± 6.7	0.978 ± 0.041
3B	14.6 ± 0.6			

surface. Although the vertical resolution is limited, there may exist a subsurface maximum of ^{137}Cs around 500 m, which may be related to the salinity minimum at 400 m (Fig. 3). More work is needed to elucidate the source and pathways of ^{137}Cs and its possible relationship with water masses there.

Prior to this study, Nagaya and Nakamura (1992) had already made some measurements of ^{137}Cs in the East China Sea. Four of their stations fall in our sampling area (Fig. 2), providing an opportunity to compare our results with theirs. All data shown in Table 4 are decay-corrected to May 30, 1999, which is our sampling date. It shows that our data and those of Nagaya and Nakamura (1992) are basically compatible, suggesting that our method for the determination of ^{137}Cs is at least as reliable as their method.

As for the spatial distribution of ^{137}Cs in the surface waters of the sampling area, the highest activity was measured at the mid-shelf station off the Changjiang Estuary. It should be noted that this station is located in a mud patch to the southwest of Jizhou Island where a cyclonic eddy of 100 km diameter exists (Hu 1984; Suk 1989; Milliman et al. 1989). Up-

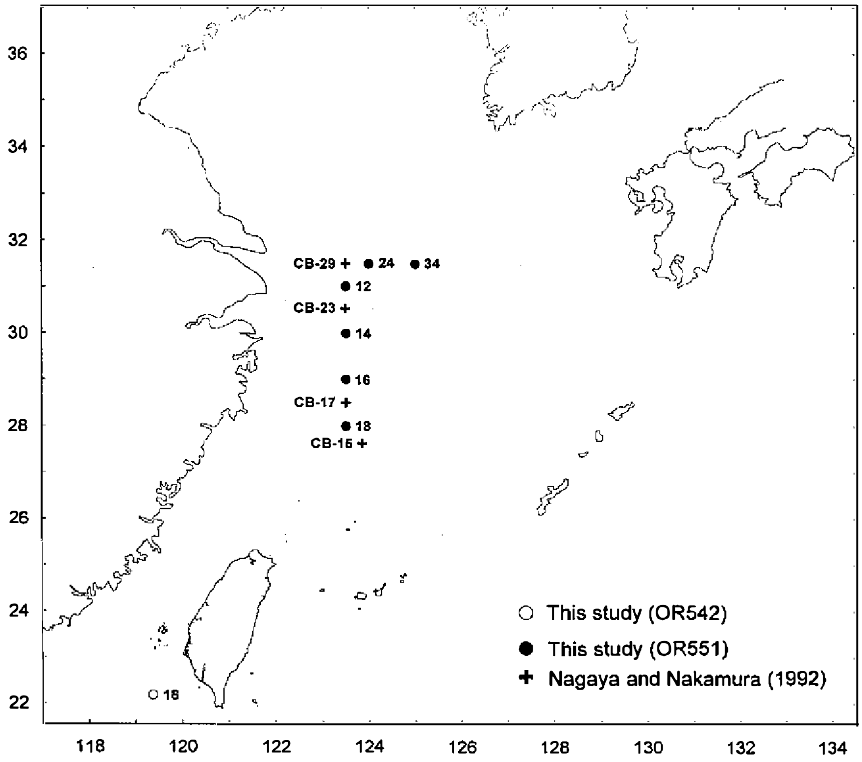

Fig. 2. Map showing sampling sites of the field experiments.

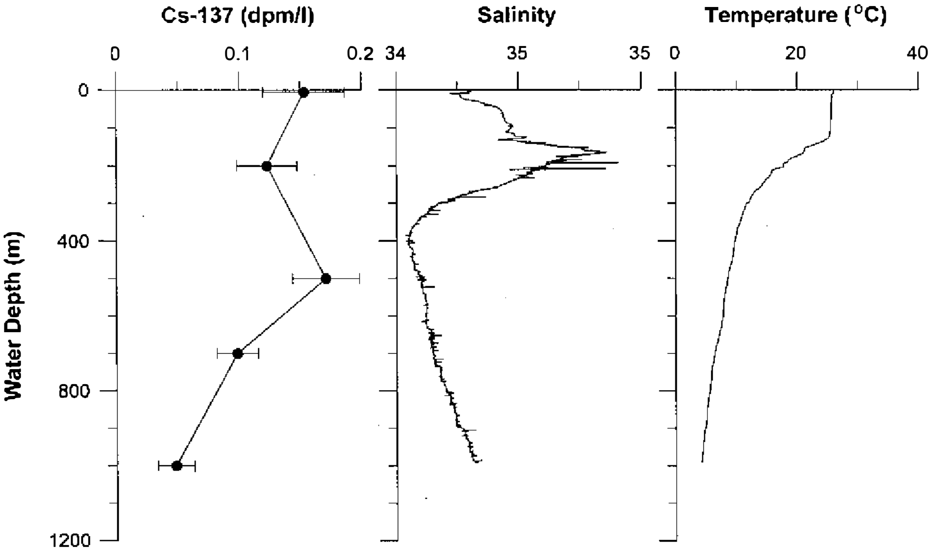

Fig. 3. Profiles of ^{137}Cs, salinity and temperature at station OR542-18.

Table 4. The adsorption efficiency of the ion-exchange columns and the activity of ^{137}Cs in the field experiments.

Sta.	Water Depth	Effic. of Column	Volumn of seawater	^{137}Cs
		%	liter	dpm
OR542-18	5m	80.91	23	0.153 ± 0.033
	200m	69.67	33.5	0.123 ± 0.025
	500m	43.53	34	0.171 ± 0.027
	700m	72.76	49.5	0.098 ± 0.017
	1000m	67.94	53	0.048 ± 0.015
OR551-12	5m	37.01	39	0.146 ± 0.016
OR551-14	5m	26.24	47	0.158 ± 0.025
OR551-16	5m	19.41	44.3	0.170 ± 0.031
OR551-18	5m	36.33	41.5	0.136 ± 0.022
OR-551-24	5m	36.68	37	0.136 ± 0.019
OR551-34	5m	22.93	52	0.176 ± 0.024
CB-15*	0m			0.124 ± 0.010
CB-17*	0m			0.116 ± 0.013
CB-23*	0m			0.134 ± 0.011
CB-29*	0m			0.143 ± 0.010

*values from Nagaya and Nakamura (1992)

welling of cold water takes place in the center of the eddy during the summer, which may very well be responsible for the observed high ^{137}Cs.

The adsorbing efficiency of the ion exchanger used in the work varies considerably and falls between 20-80% (Table 4). Thus, it may be an unreliable practice to use a single column to extract ^{137}Cs from seawater assuming that the efficiency does not change (Matsunaga et al. 1991). This is especially true for working at sea where it is difficult to maintain constant conditions at all times (e.g., filtration rate and sample size). Furthermore, it is virtually impossible to ensure that the chemical compositions of the synthesized exchangers are identical between different batches. For example, in this work, samples from the OR542 and OR551 cruises were processed using two different batches of ion exchangers; the first batch performed better than the second batch. Obviously, the amount of copper hexacyanoferrate coated on the silica gel is an important factor.

5. CONCLUSION AND SUGGESTION

Based on laboratory tests, and then field experiments, we have developed a practical method for rapid pre-concentration and determination of ^{137}Cs in seawater samples. Although the adsorption efficiency of the ion exchanger was variable and was sometimes as low as 20%, determination of ^{137}Cs is still possible if the adsorption efficiency is accurately and precisely determined using two columns in series, and with the aid of a high-efficiency HPGe detector. However, in order to save the counting time and increase the sample throughput, it is still necessary to increase the activity of ^{137}Cs adsorbed, and this may be achieved by properly adjusting the volume of seawater sample, the flow rate, and the amount of the ion exchanger.

Although more ^{137}Cs atoms can be obtained from larger samples, the study of Terada et al. (1997) showed that the adsorption efficiency of the ion exchanger would deteriorate with increasing sample volume. Therefore, an increase in sample size should be accompanied by a proportional increase in the ion exchanger volume so as to maintain the same adsorption efficiency. As for flow rate, although lower rates will in general results in higher adsorption efficiencies, it will accordingly increase the filtration time and limit the number of samples that can be processed within a certain time period. We conclude that the most sensible approach to optimize the method in the future is by increasing the amount of the ion exchanger. Fortunately, it is fairly simple to prepare the silica gel impregnated with copper hexacyanoferrates and the cost is relatively low when compared with other methods. Thus, this is a favorable method for the determination of ^{137}Cs in seawater samples.

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